PATENT COOPERATION TREATY

PCT

PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P100899WO		nt's fils reference	FOR FURTHER ACTIO	N See Notification Preliminary Ex	n of Transmittal of International camination Report (Form PCT/(PEA/416)		
				International filing date (day/m 30,10.2003	onth/yeer)	Priority date (day/month/year) 04.11.2002	
C22	International Patent Classification (IPC) or both national classification and IPC C22C30/00						
Appii DOI		TER	S LIMITED et al.				
This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.				ernational Preliminary Examining			
2.	This	REP(ORT consists of a total	of 6 sheets, including this co	ver sheet.		
	×	haar	amonded and are the	nied by ANNEXES, i.e. shee basis for this report and/or si n 607 of the Administrative Ir	neets containing	ion, claims and/or drawings which have rectifications made before this Authority the PCT).	
	Thes	e ani	nexes consist of a total	of 11 sheets.			
3.	This	repor	t contains indications re	elating to the following items:	•		
🗵 Basis of the opinion							
	11		Priority				
	111	×	Non-establishment of	opinion with regard to novel	novelty, inventive step and industrial applicability		
	IV	\boxtimes	Lack of unity of invent	tion			
	V	×	Reasoned statement	under Rule 66.2(a)(ii) with re tions supporting such statem	gard to novelty, i ent	nventive step or industrial applicability;	
ļ	1V		Certain documents di	ted	•		
	VII		Certain defects in the	International application			
	VIII		Certain observations	on the international applicati	n		
Date of submission of the demand			Da	te of completion of	this report		
01.06.2004		10	.03.2005				
Nan prei	ne and iminary	exam	g address of the internation	onal Au	thorized Officer	January S. S.	
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

I. Basis of the report

International application No.

PCT/GB 03/04665

۱.		th regard to the elements of the international application (Heplacement Sheets Which have been a foriginally filed" receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)):				
	Des	cription, Pages				
	1-25		as origi	nally filed		
	Clair	ms. Numbers				
	1-41	•	receive	d on 20.10.2004 with letter of 20.10.2004		
	Dra	wings, Sheets				
	1/B-8	3/8	as origi	nally filed		
2.	With regard to the language, all the elements marked above were available or furnished to this Authority in language in which the international application was filed, unless otherwise indicated under this item.				to this Authority in the ar this item.	
These elements were available or furnished to this Authority in the			ailable or furnish	ned to this Authority in the following language:	, which is:	
the language of a translation furnished for the purposes of t				ed for the purposes of the international search (under Rule 23.1(b)).	
				ternational application (under Rule 48.3(b)).		
		the language of a tra Rule 55.2 and/or 55.3	inslation furnish 3).	ed for the purposes of international preliminary of	examination (under	
3.	. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:			al application, the :		
		contained in the inte	mational applica	ation in written form.		
		filed together with the	e international a	application in computer readable form.		
		furnished subsequer	ntly to this Autho	ority in written form.		
		furnished subsequer	ntly to this Author	ority in computer readable form.		
		- Walter day of the displacement				
		- I I I I I I I I I I I I I I I I I I I				
4.	The	amendments have r	esulted in the c	ancellation of:		
		the description,	pages:			
	Ø	the claims,	Nos.:	42-52		
		the drawings,	sheets:			

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

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5.		This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).
		(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)
6.	Add	tional observations, if necessary:
111.	Non	establishment of opinion with regard to novelty, inventive step and industrial applicability
1.	The obvi	questions whether the claimed invention appears to be novel, to involve an inventive step (to be non- ous), or to be industrially applicable have not been examined in respect of:
		the entire international application,
	\boxtimes	claims Nos. 20,36, 38-40
		because:
		the sald international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (specify):
		the description, claims or drawings (indicate particular elements below) or said claims Nos. are so unclear that no meaningful opinion could be formed (specify):
		the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
	⊠	no International search report has been established for the said claims Nos. 21, 22,44,46,47,50 (as originally filed)
2.	or a	eaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/ mino acid sequence listing to comply with the standard provided for in Annex C of the Administrative ructions:
		the written form has not been furnished or does not comply with the Standard.
		the computer readable form has not been furnished or does not comply with the Standard.
١V	. Lac	k of unity of Invention
1.	In r	esponse to the invitation to restrict or pay additional fees, the applicant has:
		restricted the claims.
		paid additional fees.
		paid additional fees under protest.
	⊠	neither restricted nor paid additional fees.
2	. 🗆	This Authority found that the requirement of unity of Invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3	. Thi	Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3

is

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International application No.

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		complied with.			
		not complied with for the follow			
4.	Cor	nsequently, the following parts or mination in establishing this rep	of the li port:	nternational :	application were the subject of international preliminary
		all parts.			
	×	the parts relating to claims No	s. 1-19	,21-35, 37, 4	41 -
٧.	Rea cita	asoned statement under Artic ations and explanations supp	ole 35(a orting	2) with rega such stater	rd to novelty, inventive step or industrial applicability nent
1.	Şta	te ment			
	No	velty (N)	Yes: No:	Claims Claims	1-19,21-35,37,41
	Inv	entive step (IS)	Yes: No:	Claims Claims	1-19,21-35,37,41
	Ind	ustrial applicability (IA)	Yes: No:	Claims Claims	1-19,21-35,37,41
2.	Cit	ations and explanations			

see separate sheet

IN ERNATIONAL PRELIMINARY International application No. PCT/GB 03/04665 EXAMINATION REPORT - SEPARATE SHEET

- The subject-matter of claim 1 is directed to an oxide dispersion strengthened Ni-Cr-Fe alloy as defined in claim 1 (C 0.01-0.7, Si 0.1-3, 15-90 Ni, 5-40 Cr, 0.01-4.5 Hf, balance iron and imp.), having Hf as fine oxide particles and at least one carbide forming element more stable than Cr: Nb, Ti, W, Ta and Zr.
- 2. Reference is made to the following documents:

D1: EP-A-0050408

D2: US 6409847

D3: JP-A-05001355

D4: EP-A-0391381

D5: US 5851318

- 3. Novelty
- 3.1 D1 describes a Ni-Cr-Fe alloy. The composition of alloy of example C falls within the ranges as defined in claim 1 (see page 5, line 4). Alloy C contains Ti (a carbide forming element) and also 0.52 wt% Hf.

The method of producing the alloy according to the present invention is defined in claim 22. Since the method of D1 as described at page 4, line 1-12, includes the step of adding Hf before pouring as defined in claim 26, it would inevitably result in the same alloy, i.e. having at least part of Hf as oxide particles.

The subject-matter of Independent claim 1 and 22 lacks novelty over the disclosure of D1 (Art. 33.2 PCT).

Following the same approach, D1 is considered as anticipating the subject-matter of claims:

2, 4, 6, 8, 10, 15, 16, 17, 21, 41 in respect of alloy;

23,29 in respect of method;

37 in respect of the tube (pipe).

3.2 In addition, the following prior art is also considered to be novelty destroying for the cited claims:

21, 41 in respect of alloy in D2 (table 1), D3 (table 1, ex. 1-4), D4 (ex. 17, table 1), D5 (table 1, ex. A-F);

Form PCT/Separate Sheet/409 (Sheet 1) (EPO-April 1997)

IN ERNATIONAL PRELIMINARY International application No. PCT/GB 03/04665 EXAMINATION REPORT - SEPARATE SHEET

37 in respect of the tube (pipe) in D2 (claim 6), D3 (par. 18; abstract), D4 (page 5, line 32-34), D5 (col. 5, line 16-24).

The use of a rotational moulding to produce a tube is described i.e. in D2 (par. 16), D3 (par. 18), D4 (page 5, line 32-34).

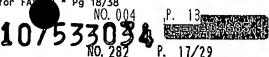
- 3.3 The subject-matter of remaining dependent claims does not appear to add any inventive features to independent claim 1 and/or 22.
- 4. The amendments made on 20.10.2004 to claims 20, 36, 38, 39, 40 are not allowable since they relate to unsearched matter either lacking unity (Rule 13.1 PCT) or undefined and obscure (Rule 6.2(a) PCT) as detailed in the International Search Report; the subject-matter of these claims is therefore not examined; the subject-matter of claims 37, 41 which refers back to any of above-mentioned claims is also not to be examined. The rest of the amendments is considered to comply with Art. 19 PCT.

Form PCT/Separate Sheet/409 (Sheet 2) (EPO-April 1997)

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CLATMS

An oxide dispersion strangthened nickel-chromiumiron alloy comprising, by weight:

5			
	Carbon	0.01 - 0.7%	
	Silicon	0.1 - 3.0%	
	Manganese	0 - 2.55	
	Nickel	15 ~ 90%	
10	Chromium	5 - 40%	
	Molybdenum	0 - 3.0%	
	Niobium	0 - 2.0\$. •
	Tantalum	0 - 2 ₋ 0€	
	Titanium	0 - 2.0%	
15	Zirconium	0 - 2.0%	
	Cobalt	0 2.0%	
	Tungsten	0 - 4.08	
	Hafnium	0.01 - 4.5용	
	Aluminium	0 - 15%	•
20	. Nitrogen	0.001 - 0.5%	
	Oxygen	. 0.001 - 0.7€	
	balance iron	and incidental	impurities,

with the proviso, that at least one carbide forming element whose carbide is more stable 25 than chromium selected from miobium, titanium, carbide tantalum and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

oxide dispersion strengthened nickel-chromiumiron alloy comprising, by weight:

0.01 to 0.5% Carbon 0.01 to 2.5% 35 5ilicon

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	Manganese	0 to 2.5%
	Nickel	15 to 50%
	Chromium	20 to 40%
	Molybdenum	0 to 1.0%
5	Niobium	0 to 1.7%
	Titanium	0 to 0.5%
	Zirconium	0 to 0.5%
	Cobalt	0 to 2.0%
	Tungsten	0 to 1.0%
10	Hafnium	0.01 to 4.5%,

balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the 15 hafnium is present as finely divided oxide particles.

An alloy according to claim 1 having the following composition, by weight:

	Carbon	0.3 to 0.7%	
	Silicon	0.1 to 2.5%	
	Manganese	2.5% max.	
	Nickel	30 to 40%	
25	Chromium	20 to 30%	
	Molybdenum	3.0% max.	
	Niobium	2.0% max.	
	Hafnium	0.01 to 4.5%	
	Titanium	0.5% max.	
30	Zirconium	0.5% max.	
	Cobalt	2.0% max.	
	Tungsten	1,0% max.	
	Nitrogen	0.001 - 0.5%	
	Oxygen	0,001 - 0.7%	
35	Balance iron	and incidental	impurities.

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An alloy according to claim 1 having the following composition, by weight:

Carbon 0.03 to 0.2% Silicon 0.1 to 0.25% 5 Manganese 2.5% max. Nickel 30 to 40% 20 to 30% Chromium Molybdenum 3.0% max. Miobium 1.7% max. 10 Hafnium 0.01 to 4.5% Titanium 0.5% max. Zirconium D.5% max. Cobalt 2.05% max. 15 Tungsten 1.0% max. Aluminium 0 - 15.0% Nitrogen 0.001 - 0.5% Oxygen 0.001 - 0.7% balance iron and incidental impurities.

An alloy according to claim I having the following composition, by weight:

	Carbon	0.3 60 0.78
25	Silicon	0,01 to 2,5%
	Manganese	2.5% max.
	Nickel	40 to 60%
	Chromium	30 to 40%
	Molybdenum	3.0% max.
30	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	1,0% max.
	Zirconium	1.0% max.
	Cobalt	2.0% max.
35	Tungsten	1.0% max

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Aluminium 0 - 15.0% Nitrogen 0.001 - 0.5% Oxygen 0.001 - 0.7%

balance iron and incidental impurities.

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6. An alloy according to claim 1 having the following composition, by weight:

0.03 to 0.2% Carbon 0.1 to 2.5% Silicon 10 2.5% max. Manganese 40 to 50% Nickel Chromium 30 to 40% Molybdenum 3.0% max. 2.0% max. 15 Niobium 0.01 to 4.5% Hafnium 0.5% max. Titanium Zirconium 0.5% max. 2.0% max. Cobalt 20 Tungsten 1.0% max., Aluminium 0 - 15,0% 0.001 - 0.5% Nitrogen 0,001 - 0.7% Oxygen balance iron and incidental impurities.

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7. An alloy according to claim 1 having the following composition, by weight:

0.3 to 0.7% Carbon 0.01 to 2.5% 30 Silicon 2.5% max. Manganese 19 to 22% Nickel Chromium 24 to 27% Molybdenum 3.0% max. 2.0% max 35 Niobium

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0.01 to 4.5% Hafnium 2.0% max. Cobalt 1.0% max., Tungsten 0 - 15.0% Aluminium 0.001 - 0.5% Nitrogen 5 0.001 - 0.7% Oxygen balance iron and incidental impurities.

An alloy according to claim 1 having the following composition, by weight: 10

	Carbon	0.03 to 0.2%		
	Silicón	0.1 to 2.5%		
	Manganesa	2.5% max		
15	Nickel	30 to 45%		
	Chromium	19 to 22%		
	Molybdenum	3.0% max.		
	Niobium	2.0% max.		
	Hafnium	0.01 to 4.5%		
20	Titanium	0.5% max.		
	Zirconium	0.5% max-		
	Cobalt	2.0% max.		
	Tungsten	1.0% max.		
	Aluminium	0 - 15.0%		
25	Nitrogen	0.001 - 0.5%		
	Oxygen	0.001 - 0.7%		
	balance iron	and incidental impurities.		

- An alloy according to any one of claims 1, 2, 3, 5, or 7, having a carbon content of from 0.3 to 0.5% by 30 weight.
 - 10. An alloy according to claim 1 or 2, having a carbon content of from 0.03 to 0.2% by weight.

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An alloy according to claim 1, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.01 to 3.0%.

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An alloy according to claim 11, in which the amount 12. of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.1% to 1.0%.

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An alloy according to claim 11 or 12, in which the 13. amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.2 to 0.5%.

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14. An alloy according to any one of the preceding claims, in which the amount of carbon in the alloy, by weight, is from 0.03 to 0.2% and the amount of hafnium in the alloy, by weight, is from 1 to 4.5%.

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An alloy according to any one of claims 1 and 4 to 15. B, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 10% and the amount of hafnium by weight is from 0.01% to 4.5%.

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16. An alloy according to claim 15, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 6% and the amount of hafnium by weight is from 0.1% to 1.0%.

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An alloy according to claim 15 or 16, in which the 17. amount of aluminium in the alloy, by weight, is from 0.1% to 4.5% and the amount of hafnium by weight is from 0.2% to 0.5%.

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- of one according to any 18. alloy precedingclaims, in which the hafnium is present in the alloy in the form of finely divided exidised particles having an average particle size of from 50 microns to 0.25 microns, or less.
- 19. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 5 microns to 0.25 microns, or less.
- an allow according to any one of the preceding following claims. having any one ο£ the compositions, by weight: 15

	Carbon	0.45%
	Silicon	1.3%
	Manganese	0.9%
20	Nickel	33.8%
	Chromium	25.7%
	Molybdenum	0.03%
	Niobium	0.85%
	Hafnium	0.25%
25	Titanium	0.1%
	Zirconium	0.01%
	Cobalt	0.04₹
	Tungsten	0.01%
	Nitrogen	0.1%
30	Iron	balance.
	Carbon	0.07\$

Silicon

Nickel

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Manganese

1.0% 0.98%

32.5%



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	Chromium	25.8%
	Molybdenum	0.20%
	Niobium	0.04%
	Hafnium	1-1%
5	Titanium	0.12%
	Zirconium	0.01%
	Cobalt	0.04%
	Tungsten	0.08#
	Nitrogen	0.1%
10	Iron	balance.

	Carbon	0.34%
15	Silicon	1.68%
	Manganese	1.10%
	Nickel	32_0₺
	Chromium	21.3%
	Molybdenum	0,01%
20	Niobium	0.80%
	Hafnium	0.25€
	Titanium	0.12%
	Zirconium	0.01%
	Aluminium	3.28€
25	Cobalt	0.04%
	Tungsten	0-01%
	Iron	balance
	Carbon	0_42%
30	Silicon	1.79%
	Manganese	1.17%
	Nickel	33.2%
	Chromium	23.3%
	Molybdenum	0.02%
35	Niobium	0.77%

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Hainium	0.24%
Titanium	0.10%
Zirconium	0.01%
Aluminium	1.64%
Cobalt	0.04%
Tungsten	0.08%
Iron	balance

- 21. An oxide dispersion strengthened nickel-chromiumiron alloy which comprises up to about 5% by weight of hafnium, with at least part of the hafnium being present as finely divided oxidised particles.
- 22. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.
 - 23. A method according to claim 22, in which the alloy is an alloy as claimed in any one of claims 1 to 21.
- 24. A method according to claim 22 or 24, wherein the hafnium particles have a particle size of less than 50 microns.
- 25. A method according to any one of claims 22 to 24, in which the amount of hafnium added to the melt is from 0.01 to 3.0% by weight.
 - 26. A method according to any one of claims 22 to 25, wherein the hafnium particles are added to the melt shortly before pouring the molten alloy into a mould.

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- 27. A method according to claim 26, in which the hafnium particles are added to the molten alloy in a ladle.
- 5 28. A method according to any of claims 22 to 27, in which the hafnium is electrolytic hafnium.
- 29. A method according to any one of claims 22 to 28, wherein the level of oxygen in the melt is varied by additions of one or more of niobium, titanium and zirconium.
- 30. A method according to claim 29, in which the titanium is added in the form of TiFe after the hafnium addition.
 - 31. A method according to any of claims 22 to 30, in which the melt temperature is in the range of from 1500°C to 1700°C.
 - 32. A method of manufacturing a corrosion resistant nickel-chromium-iron which comprises adding sequentially finely divided hafnium particles and aluminium to a melt of the alloy before pouring.
 - 33. A method according to claim 32, wherein the aluminium is added to the melt immediately before pouring the molten alloy into a mould.
- 30 34. A method according to any one of claims 22 to 33, in which the alloy is formed into a tube by rotational moulding.
- 35. A method of manufacturing a nickel-chromium-iron alloy, which comprises adding finely divided hafnium

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particles to the melt before pouring.

- A creep resistant alloy tube according to claim 42, 36. which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium.
 - A tube formed from an alloy according to any one of 37. claims 1 to 21 by rotational moulding.
 - A nickel-chromium-iron alloy having a structure and 38. described composition substantially as · illustrated in any one of Figures 1 to 4 of the accompanying Drawings, wherein the tables represent percentages by weight of the alloy constituents.
 - A nickel-chromium-iron alloy 39. having a structure and substantially as described illustrated Figures 5 or 6 of the accompanying Drawings.
- A corresion resistant tube, which comprises an exide 40. dispersion strengthened nickel-chromium-iron alloy comprising up to 15% of aluminium and up to about 5% of hafnium.
 - An alloy according to any one of claims 1 to 21, 38 41. and 35 produced by a method according to any one of claims 22 to 35.